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COPY			
(54) Title: IMAGING METHOD			
(57) Abstract			
<p>A printing method including the steps of forming an image on an imaging member, the image comprising colored polymer toner particles and a hydrocarbon liquid carrier and transferring and fusing the developed image to a paper substrate whose surface has been treated with and preferably coated with a compound having a basic functionality. The polymer is preferably an acidic polymer and the coating is preferably an imine compound.</p>			

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IMAGING METHOD

FIELD OF THE INVENTION

This application is in the field of printing and more particularly is concerned with the printing of images on coated paper.

BACKGROUND OF THE INVENTION

In U.S. Patent 5,192,638, the specification of which is incorporated herein in its entirety, Landa et al introduced a new liquid toner comprising a carrier liquid such as a light mineral oil and pigmented toner particles having fibrous extensions. The mineral oils described in the above referenced patent were Isopar L and M (TM) type saturated hydrocarbon liquids having a high Kauri-Butanol number and a high resistivity. Many other mineral oils such as Marcol 82 or other carrier liquids for liquid toner as are known in the art, are also suitable for the toner type of U.S. Patent 5,192,638, depending on the overall characteristics specified for the toner. A characteristic of these toners is that they solvate the carrier liquid at elevated temperatures but are substantially insoluble in the carrier liquid at room temperature. Other patents and publications which describe preferred embodiments of this toner type and additives useful in the toner are U.S. Patents 5,300,390; 5,286,593; 5,208,130; 5,266,435; 5,264,313; and 5,225,306 and in PCT publications WO 94/02887 the disclosures of which are incorporated herein by reference.

In U.S. Patents 5,289,238; 5,280,326; 5,276,492;; 5,270,776; 5,262,829; 5,255,508; 5,208,637; 5,166,734 and 5,148,222, the disclosures of which are incorporated herein by reference, apparatus which preferably uses these toners is described. In these references a liquid toner image comprising one of the above mentioned toners is formed on an image bearing surface and the image is transferred to a final substrate and fused thereon while it is still wet. It is a characteristic of these toners that they can generally be fused at a relatively low temperature to the paper, since

1 they solvate the carrier liquid and are thereby softened.

2 In a particularly preferred embodiment of the apparatus
3 described, the liquid toner image is transferred to an
4 intermediate transfer member from which it is transferred to
5 the final substrate. The temperature of the intermediate
6 transfer member is elevated, generally to a relatively low
7 temperature of between 85°C and 125°C and the image thereon
8 is transferred to and pressure fused to the paper by the
9 pressure of the intermediate transfer member against the
10 paper.

11 Alternatively, the liquid toner image is transferred to
12 the paper and subsequently fused thereto by the application
13 of heat with or without pressure.

14 It has been discovered that the adhesion of the toner
15 to the final substrate, while sufficient for many purposes,
16 is sometimes not sufficient for archival purposes or for
17 security purposes. Raising of the temperature of fusing does
18 not necessarily improve the adhesion to an adequate degree.

19 SUMMARY OF THE INVENTION

20 It is a purpose of the present invention to provide a
21 printing process, generally similar to the processes
22 described in the above patents and applications, for which
23 the adhesion of the image to the final substrate is
24 enhanced.

25 To this end the printing process utilizes acidic toner
26 particles and prints on paper which has a basic surface. In
27 one preferred embodiment of the paper on which the images
28 are fused has been pre-coated with a polymer having an imine
29 functionality such as polyethylene imine (anhydrous or water
30 solution), polyethylene imine epichlorohydrin (modified)
31 ethoxylated (20%) polyethylene imine or low molecular
32 weight anhydrous polyethylene imine. Alternatively other
33 materials having at least a basic functionality such as
34 polyamides can be employed. Toner images printed on paper
35 polyester or polypropylene substrates which are coated with
36 the above materials adhere much better than on untreated

1 substrates.

2 DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

3 The preferred printing method of the present invention
4 is described in the background of the invention and in the
5 prior art references which are listed therein.

6 As indicated above, the printing process of the present
7 invention is characterized by the use of paper or polymer
8 substrates which have a basic surface functionality and
9 preferably are coated with a basic compound such as an imine
10 compound, preferably a polyethylene imine compound. Such
11 basic surfaces may also be referred to as alkaline surfaces.

12 Preferred coating compounds include 20% ethoxylated
13 polyethylene imine (manufactured by Sigma), anhydrous or
14 water solutions of polyethylene imine (manufactured by BASF,
15 Arsynco or Rhome & Hass under various trade names),
16 PRIMAFLOC C-3, a low molecular weight anhydrous polyethylene
17 imine (Rhome & Hass) and epichlorohydrin polyethylene imine
18 (Sigma).

19 Other coating materials having a basic functionality
20 such as polyamides with amine and carboxylic acid
21 functionality (Macromelt 6238, 6239 and 6070 manufactured by
22 Henkel) have shown improved adhesion, especially on
23 transparencies, however, the preferred coating materials
24 show the superior adhesion enhancement.

25 The paper can be coated using any method known in the
26 art for coating such as dip coating, adding the material
27 during paper making (for example in the final bath), doctor
28 blade coating, spraying or by wire rod coating.

29 In a preferred method, polyethylene imine (50% solution
30 in water) is diluted to 1%-2% concentration by the addition
31 of isopropyl alcohol. Wire rod coating is used to coat the
32 paper with the solution. After coating the solvent is
33 evaporated by blowing warm air over the treated paper.
34 Alternatively, solutions of the material only in water or
35 only in alcohol may be used.

36 Almost all types of paper and transparencies treated

1 according to this method show improved adhesion resistance
2 (when measured using an abrasion test similar to ASTM
3 standard for CROKE meter F 1319-90, modified in that the
4 cloth is replaced by a pencil eraser). Papers which showed
5 greatly improved adhesion resistance (at least 50%-150%
6 improvement) include Krome Kote, Star white Vicksberg 110#
7 Index, Lithofect Plus Gloss White (Repap), Rayprint 110,
8 Lekyam, Neoprint, Arial Top Brilliant #1 and #2, Hammermill
9 Regalia Cover Alphe White Lustre Finish, Hammermill
10 Lazerprint, Sterling Gloss (Westvaco) and Multifect (Repap).
11 Other papers showed lesser improvement or no improvement.

12 Almost all types of papers showed substantial
13 improvement in a standard peeling test, including Star white
14 Vicksberg 110# Index, Sterling Lithosatin 110#, Lithofect
15 Plus Gloss White, Neoprint, Arial Top Brilliant #2,
16 Hammermill Regalia Cover Alphe White Lustre Finish, Warrer
17 Lustrogloss, Sterling Gloss and Multifect (Repap). Other
18 papers showed smaller or no improvement, but many of these
19 already exhibited high peel resistance.

20 The above tests were carried out utilizing pigmented
21 toners based on an ethylene terpolymer which has an acid
22 number of 60 and an ethylene copolymer which has an acid
23 number of 90. Toners based on other polymers such as some
24 Surlyn (DuPont) ionomers (for example Surlyn 8940 and Surlyn
25 8920) and IOTEK 8030 ionomer (EXXON) also showed generally
26 improved abrasion resistance and/or peel strength
27 improvement even though these polymers had a generally lower
28 acid number than the polymers used in the above tests. Some
29 toner types which are basically unusable on ordinary paper
30 become strongly adhering on paper coated according to the
31 invention.

32 The preferred toners for the printing process of the
33 present invention have the following formulations:

34 Black toner- about 16% Nucrel 925 (ethylene copolymer
35 by DUPONT), about 0.4% BT583D (blue pigment produced by
36 Cookson Pigments), about 4% Mogul L carbon black (Cabot)

1 approximately 0.45% aluminum tristearate and charge director
2 as described in US patent application 07/915,291 (utilizing
3 lecithin, BBP and ICI G3300B) and in WO 94/02887 in an
4 amount equal to 40 mg/gm of solids and the remainder Isopar
5 L.

6 Magenta toner- about 15.5% Bynell 2002 (ethylene
7 terpolymer by DUPONT), about 2.8% Finess Re F2B magenta
8 pigment (Toyo Ink), about 0.14% Sico Fast Yellow D1355DD
9 yellow Pigment (BASK) approximately 0.45% aluminum
10 tristearate and charge director as described in US patent
11 application 07/915,291 (utilizing lecithin, BBP and ICI
12 G3300B) and in WO 94/02887 in an amount equal to 40 mg/gm of
13 solids and the remainder Isopar L.

14 Cyan toner has a composition similar to that of the
15 magenta toner except that 2.36% of BT583D pigment (Cookson
16 replaces the magenta pigment and the yellow pigment is
17 reduced to 0.03%. The composition of the yellow toner is
18 similar to that of the black toner except that 3.13% of
19 yellow pigment is substituted for the pigment and carbon
20 black of the black toner.

21 It will be appreciated by persons skilled in the art
22 that the present invention is not limited by the description
23 and example provided hereinabove. Rather, the scope of this
24 invention is defined only by the claims which follow:

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CLAIMS

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2 1. A printing method comprising:
3 forming an image on a imaging member, the image
4 comprising colored polymer toner particles and a hydrocarbon
5 liquid carrier; and
6 transferring and fusing the developed image to a paper
7 substrate whose surface has been treated with a compound
8 having a basic functionality.
9
- 10 2. A printing method comprising:
11 forming an image on a imaging member, the image
12 comprising colored polymer toner particles and an oily
13 liquid carrier; and
14 transferring and fusing the developed image to a paper
15 substrate whose surface has been treated with a compound
16 having a basic functionality.
17
- 18 3. A printing method according to claim 1 or claim 2
19 wherein the treatment of the surface comprises coating the
20 surface with the compound.
21
- 22 4. A printing method according to any of the preceding
23 claims wherein the compound is a basic compound.
24
- 25 5. A printing method according to any of the preceding
26 claims wherein the colored polymer toner particles are
27 acidic in nature.
28
- 29 6. A printing method according to any of the preceding
30 claims wherein the polymer comprises an ethylene terpolymer
31
- 32 7. A printing method according to any of claims 1-
33 wherein the polymer comprises an ethylene copolymer.
34
- 35 8. A printing method according to any of claims 1-
36 wherein the polymer comprises an ionomer.

1

2 9. A printing method according to any of the preceding
3 claims wherein the compound comprises an imine compound.

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5 10. A printing method according to claim 9 wherein the
6 imine compound comprises a polyethylene imine compound.

7

8 11. A printing method according to claim 9 wherein the
9 imine compound comprises an ethoxylated polyethylene imine.

10

11 12. A printing method according to claim 9 wherein the
12 imine compound comprises a epichlorohydrin polyethylene
13 imine.

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15 13. A printing method according to any of the preceding
16 claims wherein the liquid carrier is a saturated
17 hydrocarbon.

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INTERNATIONAL SEARCH REPORT

Application No
PCT/NL 94/00204

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03G7/00 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03G B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 035 845 (NIHON JUNYAKU) 25 June 1980 see page 1, line 22 - line 38 see page 3, line 4 - line 10 ---	1-4,9,10
X	EP,A,0 566 270 (XEROX) 20 October 1993 see column 4, line 10 see column 5, line 4-11 see column 16, line 46 ---	1,3,4, 9-12
X	EP,A,0 469 595 (XEROX) 5 February 1992 see claims 1,5,8 ---	1,3,4, 9-12
X	EP,A,0 194 776 (3M) 17 September 1986 see examples 3,4 ---	1,3,4,7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,30 42 296 (KOSCHE) 9 June 1982 see claims 1,4,5	1-13
A	FR,A,2 574 571 (SAVIN) 13 June 1986 cited in the application see claims 1,13,16	1,5-8,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 94/00204

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2035845	25-06-80	JP-A- 54133136 WO-A- 7900898	16-10-79 15-11-79
EP-A-566270	20-10-93	US-A- 5212008 JP-A- 6040146 US-A- 5320902	18-05-93 15-02-94 14-06-94
EP-A-469595	05-02-92	US-A- 5277965 JP-A- 5096843	11-01-94 20-04-93
EP-A-194776	17-09-86	AU-B- 581957 AU-A- 5298886 CA-A- 1251827 DE-A- 3681942 JP-A- 61205954 KR-B- 9404213	09-03-89 11-09-86 28-03-89 21-11-91 12-09-86 17-05-94
DE-A-3042296	09-06-82	NONE	
FR-A-2574571	13-06-86	CA-A- 1264592 CH-A- 673342 DE-A- 3543302 GB-A, B 2169416 GB-A, B 2176904 JP-C- 1879076 JP-B- 5087825 JP-A- 61180248 US-A- 5407771 US-A- 4794651 US-A- 5264313 US-A- 5192638	23-01-90 28-02-90 12-06-86 09-07-86 07-01-87 07-10-94 20-12-93 12-08-86 18-04-95 27-12-88 23-11-93 09-03-93